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Hydrogen bonding in neat aliphatic alcohols: The Gibbs free energy of self-association and molar fraction of monomer

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ABSTRACT

The magnitudes of the Gibbs free energies of self-association for several primary aliphatic alcohols at 298 K are calculated. The fraction of monomeric molecules in bulk alcohols is determined. We started from the experimental data on the Gibbs free energies of vaporization of alcohols, and quantified the contributions from three types of solvation effects: non-specific van der Waals interactions, solvophobic effects, and hydrogen-bonding processes (self-association) using an extrathermodynamic approach. Calculated values for monomer fractions are compared and found to be in general agreement with the results obtained from various association models: CPA, NRHB, sPC-SAFT, and other data reported in literature. The influence of hydrogen bond cooperativity on the process of self-association is shown.

1. Introduction

The process of self-association of aliphatic alcohols has attracted attention of scientists for a long time [1]. Simple molecules forming intermolecular hydrogen bonds are considered as convenient models that should help us to understand noncovalent binding processes in complicated biological and supramolecular systems. The energetic and structural properties of associates, dynamics of association processes have been extensively studied in neat monohydric aliphatic alcohols and their mixtures with other organic substances using thermodynamic [2–5], spectroscopic [6–8], and theoretical [9–11] methods. A large number of semi-empirical models for the association process were suggested [3–5,12–15].

There is a huge number of possible structures of alcohol associates, but in the simplest models of association process the number of considered associates is limited (e.g. only monomeric molecules and cyclic tetrameric associates are considered [16]). Less strict limitation used in many advanced models is that there may exist associates of any size, but the thermodynamic functions of H-bond formation are the same for all H-bonds either there is only a small number of H-bond types which differ by their energies. It is well-known that real hydrogen-bonding processes are cooperative [17–19]. The enthalpy and Gibbs energy of dimerization of alcohols are significantly less negative than that of addition of the third and subsequent monomeric molecules to the associate, and the corresponding constants of association are larger in magnitude [20–23]. Thus, at least two different values of each thermodynamic function – one for dimerization and one for subsequent self-association – are required to describe the process of association in realistic models.

In a number of spectroscopic studies, a simplified classification of the types of alcohol molecules and their OH groups that does not take cooperative effects into account is used [7]. Free monomer molecules and their hydroxyls are called type α, type β is for terminal free OH groups, γ for OH groups with non-H-bonded lone pair electrons of oxygen, and δ for molecules bonded with other alcohol molecules from both sides. All the molecules or bonds of each type are assumed to have similar OH frequencies in vibrational spectra and similar values of partial molar thermodynamic functions (enthalpy, Gibbs energy, entropy). In literature, the fractions of α–γ types in neat alcohols are obtained as a result of analysis of experimental data on the basis of various model assumptions.

2. Methodology

2.1. Gibbs energy and monomer fraction

Nevertheless, it is possible to characterize the thermodynamics of association processes in neat alcohols without any arbitrary assumptions about the energies of association and the structure of associates. One may use average thermodynamic function of association $\Delta_{ass}f^{ROH}(f=G,H,S)$ which reflects the change in the Gibbs energy, enthalpy, or entropy when one mole of alcohol ROH is changing from its monomeric state in the neat phase into the equilibrium mixture of associates that forms the same neat phase. In other words, the initial state of considered process is the monomer diluted in the bulk alcohol with the certain standard concentration

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